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13. ABSTRACT (Maximum 200 words) Our work moved along three directions whose choice was made in order to increase our understanding of the concepts of molecular energy content and stability. The direction involved first the computation of accurate adiabatic potential energy surfaces (PES) and vibrational analysis of high energy content clusters in ground and excited states in geometries of intramolecular charge transfer which give rise to closely avoided regions. These geometries are predicted a priori according to our published maximum ionicity in the excited state (MIES) theory. The clusters and molecules which were studied were $H_2$ , $(H_2)_2$ , $H_3$ , $(H_2O)_2$ and $H_3O_2$ . The publications which resulted from these studies are given in 1-4. The second research activity had as its object the development and application of efficient methods for the computation of predissociation lifetimes due to the nonadiabatic coupling of the PES computed in part one. As a result, we learned that the lifetime of $H_4$ due to its ./. .					
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nonradiative coupling with the ground hypersurface leading to  $H_2+H_2$  is of the order of  $10^{-13}$  s. Our related publication is ref.5.

Finally, the third activity opened the direction of the study of molecules and clusters in ionic crystals. Our intention was to determine quantitatively the degree of possible perturbations by the surrounding solid medium on the molecular energy spectra and on the stability of the corresponding states. Novel results emerged. These are presented -together with the theoretical models- in refs.6-8.

#### References

1. C.A.Nicolaides, J.Mol.Str.(Theochem.) 202 285 (1989)
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## Final Scientific Report

C.A. Nicolaides

The research which was supported by the AFOSR grant 87-0348 aimed at the qualitative and quantitative understanding of situations where electronic excited states of molecules and clusters become bound in unusual geometries and decay to a ground repulsive hypersurface via nonradiative couplings. The energy and stability studies were done for free molecules as well as for molecules embedded in ionic crystals.

Apart from the enormous unpublished computational work that was accomplished as tests of the various conceptual approaches and methods, a number of problems were examined and the results were published. Below we give the corresponding titles and short summaries.

### 1. Chemically Bound Excited Clusters

C.A. Nicolaides, J.Mol.Str.(Theoch.) 202 (1989) 285.

According to the conventional understanding of their electronic structure, polyatomic clusters of "non-reactive" closed shell molecular fragments have been considered as undergoing exclusively van der Waals bonding, even when excited. Since 1983, new results and proposals have been presented regarding such clusters. These refer to the existence of chemical bonding in excited states, caused by charge transfer and overlap effects in unusual geometries. Directly related to these developments is the study of  $\text{He} + \text{H}_2^+$  collisions and of fluorescence quenching of the  $\text{H}_2\text{B}^+ \Sigma_u^+$  state by the noble gases. It is reasonable to expect that there exist a number of such situations and that they may play an important role in the storage and distribution of energy in the molecular, liquid or

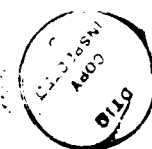
solid state.

The CBEC are formed in geometries which can be predicted semiquantitatively according to the maximum ionicity excited state (MIES) theory of bonding. This theory predicts chemical (e.g. larger than 1 eV) minima in excited states of clusters of normally non-interacting species by relating the binding and the corresponding geometry to the strong charge transfer which occurs in one of the molecular constituents of the cluster, in its excited state. In its equilibrium configuration, this constituent is bonded mainly covalently. For example, in the case of

$H_2^+ B^1 \Sigma_u^+$ , the equilibrium geometry is at  $2.4 a_0$ , whereas the geometry of the MIES is around  $4.0 a_0$ . The stability of the CBEC, depends on the transition probability of two types of decay modes. The first is the radiative one. It is expected to be relatively slow since, on the one hand at the same geometry the energy difference between the surfaces is very small (avoided crossing), while, on the other hand, at the dissociation limit of two ground state molecules the geometrical differences are large and yield a very small vibrational functions overlap.

Of course, the determination of the exact magnitude of the radiative decay requires a complete calculation of the integrated emission transition probability.

The second decay mode is the radiationless fragmentation via the non-adiabatic vibronic coupling between the surfaces. It constitutes the physically important mechanism for the release of the energy of the CBEC. Given the original work on the CBEC, understanding the dynamics of this mechanism and deducing the lifetime of  $H_4^+$  has been of considerable scientific and technological interest. Calculations suggest that its lifetime is of the order of  $10^{-13}$  s. Since this is a very short lifetime, direct observation of the  $H_4^+$  CBEC and its dynamics is very difficult. However, in recent results of  $H_2^+$  and  $H_4^+$  in ionic crystals, it is found that the effect of crystals such as AgF and RbI on the spectra and the energy surface characteristics of  $H_2^+$ ,  $H_4^+$  and of similar excited molecules, is very large. This finding suggests that, with a suitable selection of solid media, it may



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become possible to manipulate substantially the electronic spectroscopy and the energy storage and dissipation of certain classes of molecules and clusters.

## 2. On the stability of excited tetrahydrogen

A. Metropoulos and C. A. Nicolaides,

J. Phys. B: At. Mol. Opt. Phys. **21** (1988) L77-L81.

Using the MIES model, Metropoulos and Nicolaides (1987) found an approximate geometry for the minimum of the  $H_4$  "excimer" state in a trigonal pyramidal geometry lying near an avoided crossing with the ground state. This minimum occurs in a  $C_s$  symmetry when the base of the pyramid is an isosceles triangle with each of the equal sides having a length of  $1.8 a_0$  while the third side has a length of  $1.65 a_0$ . The distance of the H atom at the apex of the pyramid ( $H_a$ ) from its base is  $4.2 a_0$ . Now, according to the MIES model the minimum should occur in a  $C_{3v}$  symmetry. However, in this symmetry there is a conical intersection between the lowest  $^1A$  and  $^1E$  states at the position of the expected minimum and, when in such a geometry, the cluster dissociates. However, when the symmetry changes from  $C_{3v}$  to  $C_s$  by distorting the equilateral base of the pyramid to an isosceles triangle one obtains a true avoided crossing giving rise to a true minimum for the excimer state. The distance of the  $C_s$  minimum from the conical intersection is about 72 meV and it does not support any vibrational level.

By further optimization we have obtained a minimum of the  $A\ ^1A'$  excited state of the  $H_4$  cluster in a  $C_s$  trigonal pyramidal geometry, which can support at least one vibrational level. This minimum is near an avoided crossing with the ground  $1A'$  state. The non-adiabatic matrix elements of their vibronic coupling along a possible dissociation coordinate were also calculated.

### 3. An Estimate of the Lifetime of Excited Tetrahydrogen

I.D. Petsalakis, A. Metropoulos, G. Theodorakopoulos and C.A. Nicolaides,  
Chem. Phys. Letts. 158 (1989) 229.

The geometry of the chemically bound excited cluster (CBEC)  $H_4$  has been found to be pyramidal with a  $C_{2v}$  triangular basis and overall  $C_s$  symmetry belonging to the  $A'$  irreducible representation, near a very narrow avoided crossing with the dissociative  $A'$  ground state. In order to explore the stability of this CBEC state, the zeroth vibrational level for the local mode involving motion of the H atom at the apex of the pyramid, towards and away from the triangular basis (R coordinate) has been determined assuming all other nuclear motions frozen. This level is about  $518\text{ cm}^{-1}$  lower than a nearby conical intersection, which occurs when the triangular base assumes  $C_{3v}$  symmetry.

Within this  $H_3$ -H diatom approximation,  $H_4^*$  ( $v=0$ ) can make a transition to the dissociative ground state ( $H_2+2H$ ) either non-radiatively via vibronic coupling in the region of the avoided crossing, or radiatively (a much slower process).

Using analytic as well as numerical methods, the upper bound to the lifetime of the  $H_4$  chemically bound excited cluster has been computed to be of the order of  $10^{-13}$  s.

### 4. Structure and Vibrational Analysis of Protonated Hydrogen Peroxide.

P. Valtazanos, E.D. Simandiras and C.A. Nicolaides  
Chem. Phys. Letts. 156 (1989) 240.

According to the (MIES) theory one possible CBEC is that of  $(H_2O)_2$ . The location of the equilibrium geometry of the protonated hydrogen peroxide cation would seem like a logical first step in such an investigation. Moreover,  $H_3O_2^+$  is known to exist experimentally, but no theoretical or experimental data regarding its geometry or vibrational spectrum are available. In contrast, a vast

quantity of experimental data exist for hydrogen peroxide, allowing theoretical investigations of this molecule to be validated as to their accuracy.

We have determined the geometry and vibrational spectrum of the protonated hydrogen peroxide cation by ab initio calculations at the SCF, FORS-MCSCF and second-order Moller-Plesset (MP2) levels. The methods used were tested by similar calculations on  $\text{H}_2\text{O}_2$  and comparison of these results with experimental values. It was found that both the FORS-MCSCF and MP2 methods gave very good (and similar) results while -predictably- the SCF results were poor. The  $\text{H}_3\text{O}_2^+$  geometry turns out to be almost that which can be generated from  $\text{H}_2\text{O}_2$  by a reflection in one of the OOH planes.

#### 5. The $(\text{H}_2\text{O})_2^*$ Cluster at a Geometry of Intramolecular Charge Transfer

C.A. Nicolaides, and P. Valtazanos

Submitted to Chem.Phys.

We have computed the potential energy surfaces (PES) of a chemically bound excited state of the  $(\text{H}_2\text{O})_2^*$  cluster (10.0 eV above the energy of two  $\text{H}_2\text{O}$  molecules) and of the corresponding dissociative ground state at a geometry which was predicted by applying the maximum ionicity of excited state (MIES) theory of bonding. These PES confirm the existence of an avoided region which is caused by intramolecular charge transfer and is characteristic of the MIES structures. Three dimensional PES plots show the overall repulsive nature of the lower state, which breaks into  $(\text{H}_2\text{O})+(\text{H}_2\text{O})$ . Also, by taking a slice of the two surfaces along the fragmentation coordinate for  $[\text{H} \cdots^{\text{R}} \cdots \text{H}_3\text{O}_2]$ , the two dimensional MIES feature of an avoided crossing is brought out and connection is made with structure and PES characteristics of certain diatomic molecules where bonding due to charge transfer is recognized from the charged atomic dissociation products. The present results, together with our earlier ones on clusters such as  $(\text{H}_2)_n$  and  $\text{XH}_2$  ( $\text{X}=\text{He}, \text{Ne}, \text{Ar}$ ), suggest that the features associated with

MIES structures should form part of our description of electronic structure and of intramolecular dynamics of a number of nonreactive closed shell species.

#### **6. Excited Molecules and Clusters in Solid Media. Hydrogen and Tetrahydrogen in Ionic Crystals.**

C.A. Nicolaides, P. Valtazanos and N.C. Bacalis

Chem.Phys.Letts. 151 (1988) 22.

We present accurate results from full CI calculations on ground and excited states  $H_2$  and  $(H_2)_2$  embedded in AgF and RbI solids. The physical problem has been reduced to a large cluster calculation where the solid medium is represented by its effective potential. In the case of strongly ionic crystals, this can be achieved by the use of point charges. In other situations, or in more refined calculations, the potential due to the medium can be obtained from solid-state quantum-mechanical calculations. In order to draw reliable conclusions about the characteristics of the CBEC, especially in regions of avoided crossings with the repulsive ground state, the problem was treated at the full CI level. It is found that the effect of these crystals on the spectra and on the energy surface characteristics is considerable. This finding suggests that, with a suitable selection of solid media, it may become possible to manipulate substantially the electronic spectroscopy and the energy storage and dissipation of certain classes of molecules and clusters.

#### **8. Hydrogen Molecule and Tetrahydrogen Cluster embedded in Ionic Crystals.**

P. Valtazanos, N.C. Bacalis and C.A. Nicolaides

Chem. Phys. 1990, in press.

We have computed the ground and low-lying excited states of the hydrogen molecule and of the chemically bound excited tetrahydrogen embedded in various NaCl-type crystals, by full configuration-interaction calculations. The excited states are affected considerably by such an environment. We have also



estimated the effects of the ionic environment on the lifetime of  $H_4^+$ , which is due to the nonadiabatic coupling between the first excited and the ground hypersurfaces. Application of concepts from the Landau-Zener model shows that the lifetime remains in the order of  $10^{-13}$  sec, as computed earlier for the free molecular state.

#### **8. Inversion of Molecular Spectra by Solid Environments**

C.A. Nicolaides and P. Valtazanos

Submitted to Chem.Phys.Lett.

It was demonstrated via full CI cluster calculations of  $H_2$  in a NaF crystal that it is possible for spectra of molecules embedded substitutionally in ionic crystals to be inverted as compared to those of the free state. Such inversions imply, in principle, the possibility of switching mechanisms of large amounts of molecular energy as a function of crystal distortion.

**Research Grant: AFOSR-87-0348  
Completed Project Summary**

**Title:** Potential Energy Surfaces and Stability of High Energy Content Excited Bound Clusters

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**Inclusive dates:** August 1, 1987 - March 31, 1990

**Publications:**

1. C.A. Nicolaides, J.Mol.Str. (Theochem) 202 285 (1989)
2. A. Metropoulos and C.A. Nicolaides, J.Phys. 21 L77 (1988).
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The (CBEC) chemically bound excited clusters are formed in geometries which can be predicted semiquantitatively according to the maximum ionicity excited state (MIES) theory of bonding. This theory predicts chemical (e.g. larger than 1 eV) minima in excited states of clusters of normally non-interacting species by relating the binding and the corresponding geometry to the strong charge transfer which occurs in one of the molecular constituents of the cluster, in its excited state. In its equilibrium configuration, this constituent is bonded mainly covalently. For example, in the case of  $H_2^*B^1\Sigma_u^+$ , the equilibrium geometry is at  $2.4 a_0$ , whereas the geometry of the MIES is around  $4.0 a_0$ . Two CBECs were studied extensively.  $(H_2)_2^*$  and  $(H_2O)_2^*$ .

The physically important mechanism for the release of the energy of the CBEC, is via the nonadiabatic coupling with the ground hypersurface. Calculations on tetrahydrogen based on our theoretical developments suggest that its lifetime is of the order of  $10^{-13}$  s. Since this is a very short lifetime, direct observation of the  $H_4^*$  CBEC and its dynamics is very difficult. However, in recent results of  $H_2^*$  and  $H_4^*$  in ionic crystals, it is found that the effect of crystals such as AgF and RbI on the spectra and the energy surface characteristics of  $H_2^*$ ,  $H_4^*$  and of similar excited molecules, is very large. This finding suggests that, with a suitable selection of solid media, it may become possible to manipulate substantially the electronic spectroscopy and the energy storage and dissipation of certain classes of molecules and clusters.